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Assessing Anthropogenic Impacts on Chemical and Biochemical Oxygen Demand in Different Spatial Scales with Bayesian Networks

Jing Xu [1,2], Guangqiu Jin [1,2,*], Yuming Mo [1,2], Hongwu Tang [1,2] and Ling Li [3]

1 State Key Laboratory of Hydrology-Water Resource and Hydraulic Engineering, Hohai University, Nanjing 210098, Jiangsu, China; xujinghhu@hhu.edu.cn (J.X.); yuming_m@hhu.edu.cn (Y.M.); hwtang@hhu.edu.cn (H.T.)

2 College of Water Conservancy and Hydropower Engineering, Hohai University, Nanjing 210098, Jiangsu, China

3 School of Engineering, Westlake University, Hangzhou 310024, Zhejiang, China; liling@westlake.edu.cn

* Correspondence: jingq@hhu.edu.cn; Tel.: +86-25-83787125

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Abstract: In order to protect the water environment in seriously polluted basins, the impacts of anthropogenic activities (sewage outfalls and land use) on water quality should be assessed. The Bayesian network (BN) provides a convenient way to model these complex processes. In this study, anthropogenic impacts on chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were evaluated in the Huaihe River basin (HRB) considering dry and wet seasons and different spatial scales. The results showed that anthropogenic activities had the most significant impacts on COD and BOD at the catchment scale. In dry seasons, sewage outfalls played an important role in organic pollution. Farmland became the most important source in wet seasons although it had a "sink" process in dry seasons. Intensive human activities in urban made significant contributions to increased COD levels. Grassland had a negative relationship with organic pollution, especially in dry seasons. Therefore, governments should implement strategies to control organic matters transported from urban and farmland regions. Increasing the efficiency of wastewater treatments and the percentage of grassland in the riparian zone could improve water quality. These results can enhance understanding of anthropogenic impacts on water quality and contribute to efficient management for river basins.

Keywords: chemical oxygen demand (COD); biochemical oxygen demand (BOD); anthropogenic activities; spatial scales; Bayesian networks

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1. Introduction

The intensive anthropogenic disturbance degrades water quality and causes many environmental problems, such as eutrophication in rivers, hypoxic/anoxic episodes in bottom water, increased toxicity to aquatic organisms and declines in aquatic biodiversity [1–3]. Water pollution has become a global environmental problem and poses severe risks to human and aquatic ecosystem health [4–6]. Contaminants come from both point and nonpoint sources, which are discharged into receiving water by sewage outfalls and transported to rivers by surface runoff from urban or agricultural lands, respectively [7,8]. Consequently, many influence factors are related to the complex processes between anthropogenic activities and water quality degradation. It is urgent to implement efficient and effective strategies for better management of river basins based on scientific assessments of anthropogenic impacts.

Researchers have analyzed the impacts of different human activities on water quality, such as agricultural fertilization, loss of woodland and grassland, urbanization and contaminations from domestic and industrial wastewater [9,10]. Spatial variations of anthropogenic activities may cause a different distribution of land use across the whole river basins [11]. Although some previous studies only focused on a single spatial scale when analyzing the effects of human activities on water quality [12–14], some other research took the different spatial scales, from local scales to the whole catchment scale, into consideration [15–17]. Their results suggested that water quality indicators tend to have the most significant correlation to land use in different spatial scales, which were caused by various catchment characteristics and climate conditions between them [18–21]. Finding the spatial scale at which human activities have the most significant effects on water quality is going to make it more likely that we can identify the priority regions in the river basin and then guide the more efficient water protection policies. Besides, when comparing previous researchers, their results implied that one specific land use type may have various levels of effects even inversed influence on water quality in dry and wet seasons [22–24]. Therefore, it is important to comprehensively considered different spatial scales and seasons when assessing the effects of sewage outfalls and land use on water quality.

The Huaihe River Basin (HRB) is a highly polluted river basin in China due to rapid social development and intensively anthropogenic activities [25,26]. As a result, several serious water pollution incidents occurred in this area, which risked the drinking water safety of 10 million people living alongside the rivers, especially in the 1990s [23,27,28]. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were selected to be typical water quality indicators to analyze, while COD is an indicator of the mass of oxygen consumed by organic pollutants and BOD is the amount of oxygen needed by aerobic biological organisms breaking down organic matters. The two parameters reflect the levels of oxygen-consuming organic pollution in the water body and are used as the main criteria for aquatic ecosystem resources assessment [29–31]. Moreover, COD was the most severe water pollution in the HRB based on previous studies [32,33].

In the research, the impacts of human activities (land use and sewage outfalls) on COD and BOD in the HRB were assessed in dry and wet seasons and different spatial scales (from local to catchment scales). In order to conveniently model the complex processes between anthropogenic activities and water quality, Bayesian networks (BNs) were applied, which can decompose the global model distribution of all variables into the local conditional probability distribution of each variable by the directed acyclic graph (DAG) [34–36]. In this way, both quantitative variables (such as water quality and land use data) and qualitative variables (different season scenarios) can be easily incorporated into one model. Moreover, the DAG can provide the visual interpretation of model structures in the complex system, which contributes to a more understandable model about influence factors on water quality in river systems [37].

The main aims of this paper are to: (1) develop the BN models to describe anthropogenic impacts (sewage outfalls and land use) on COD and BOD in dry and wet seasons in the HRB across different spatial scales; (2) find out the spatial scale in which anthropogenic activities have the most significant effects on COD and BOD; (3) assess the contribution of anthropogenic activities in both dry and wet seasons. This study will improve the understanding of the anthropogenic impacts on water quality in the HRB, which is crucial for efficient water environment protection.

2. Materials and Methods

2.1. Study Area and Monitoring Stations

2.1.1. Study Area

The HRB (longitudes 112–121° E and the latitudes 30–36° N) is a seriously polluted river basin in eastern China, whose drainage area is about 270,000 km^2 (Figure 1a). The origination of the HRB is the Tongbai Mountain in Henan province, then the main section of the Huaihe River (MRHR) runs from west to east before discharging into the Hongze Lake (Figure 1b). The annual precipitation is about 900 mm which has unevenly intra-annual and interannual distribution, accordingly, about 74% precipitation was observed in wet seasons [38–41].

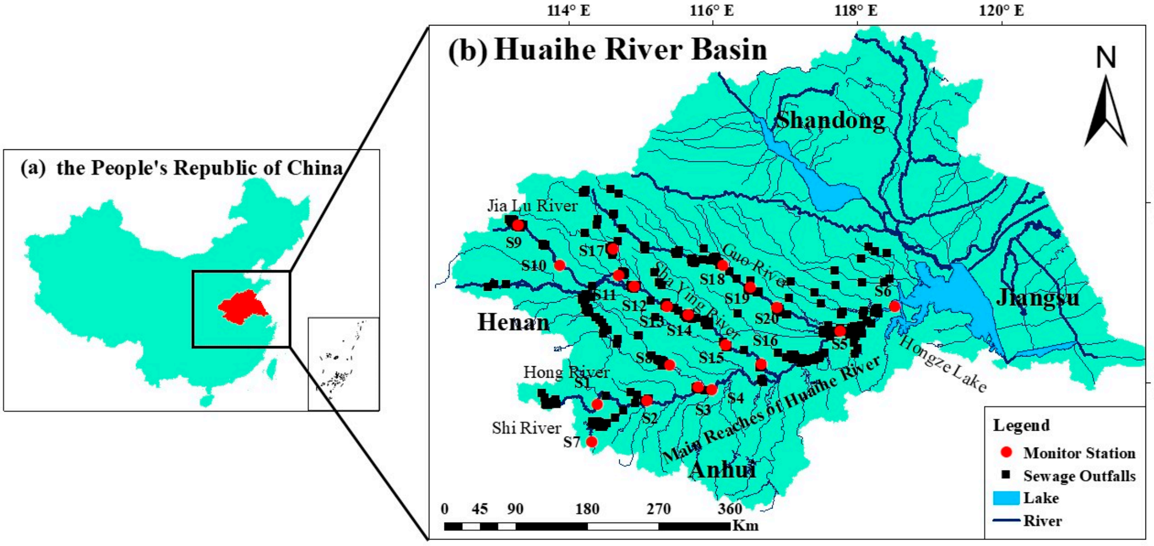

Figure 1. (**a**) The map of the People's Republic of China. The red part is the location of the Huaihe River Basin (HRB). (**b**) The locations of monitor stations and sewage outfalls in the HRB.

Due to rapid urbanization and industrialization, the constructions of environmental infrastructure were not enough to match the socio-economic development in the HRB, specifically, the percentage of treated wastewater was less than 50% by 2005 [42,43]. Therefore, large amounts of contaminants from point sources were discharged into the waterbody, such as coal-fired power plants, industrial runoff and domestic sewage outfalls. Besides, based on the climate condition and crop characteristics, the dominant crops in the HRB include paddy, maize and wheat. The growth periods of paddy and maize are similar, which are from April to October, while the growth period of wheat is from October to May [44,45]. In order to increase crop yields, excessive fertilizer and pesticides were applied by farmers during crop growth periods [46,47]. Thus, nonpoint sources resulting from agricultural fertilizers and soil erosion have greatly degraded the water environment and caused serious pollution incidents in this area [32,48,49].

2.1.2. Monitoring Stations

There are twenty monitoring stations included in the research area (Table 1). Six of them (S1–S6) are lying in the MRHR, while the others are in tributaries. Eight stations (S9–S16) and three stations (S18–S20) are lying in two major tributaries in the HRB, Shaying River (SYR) and Guo River (GR), respectively. The other three stations are in the Shi River (SR), Hong River (HR) and Jialu River (JLR), respectively.

Table 1. The summary of twenty monitor stations in the manuscript.

Station Name	Station Code	Location	Longitude (° E)	Latitude (° N)
Changtaiguan	S1	Main reaches of Huaihe River	114°4′	32°19′
Xixian	S2	Main reaches of Huaihe River	114°44′	32°20′
Huaibin	S3	Main reaches of Huaihe River	115°25′	32°26′
Wangjiaba	S4	Main reaches of Huaihe River	115°36′	32°26′
Wujiadu	S5	Main reaches of Huaihe River	117°22′	32°57′
Xiaoliuxiang	S6	Main reaches of Huaihe River	118°8′	33°10′
Tanjiahe	S7	Shi River	113°58′	31°54′
Bantai	S8	Hong River	115°4′	32°43′
Gaocheng	S9	Shaying River	113°8′	34°24′
Huaxing	S10	Shaying River	113°40′	33°55′
Huangqiao	S11	Shaying River	114°27′	33°46′
Zhoukou	S12	Shaying River	114°39′	33°38′
Huaidian	S13	Shaying River	115°5′	33°23′
Jieshou	S14	Shaying River	115°21′	33°16′
Fuyang	S15	Shaying River	115°50′	32°54′
Yingshang	S16	Shaying River	116°17′	32°39′
Fugou	S17	Jialu River	114°24′	34°4′
Boxian	S18	Guo River	115°52′	33°48′
Guoyang	S19	Guo River	116°13′	33°31′
Mengcheng	S20	Guo River	116°33′	33°17′

2.2. Data Sources and Processing

The datasets of COD and BOD concentration and the amount of COD and BOD contaminants from sewage outfalls (including domestic and untreated or partly treated industrial wastewater) were collected from the Huaihe River Water Resource Protection Bureau. The water samples were collected weekly or monthly to measure COD and BOD concentration from 2000 to 2013. All measurements of water quality indicators were measured according to the national standard methods of water quality testing [50,51]. The daily discharge datasets were provided by the hydrographic office of Huaihe River Commission of the Ministry of Water Resources, P. R. C. The COD and BOD loads were calculated by concentration data to multiply the discharge data in the same days. Based on the climate characteristics in the HRB [52,53], the dry seasons were from October to March and the wet seasons were from April to September. In order to assess the anthropogenic impacts on water quality in dry and wet seasons, the annual average of COD and BOD loads in two seasons were calculated.

The spatial datasets, including the digital elevation model (DEM) at 90 × 90 m resolution and map of land use types in 2005, 2010 and 2015, were collected from the Data Centre for Resources and Environmental Science of the Chinese Academy of Sciences (see http://www.resdc.cn). Based on the Gauss–Kruger projected coordinate system, the locations of monitoring stations, stream networks, land use maps and DEM data in the HRB were transformed into spatial layers by ArcGIS (380 New York Street, Redlands, ESRI Company, CA, USA). Each monitoring station was set to be the outlet point for the corresponding sub-catchment. Therefore, based on stream networks, locations of monitor stations and topographical features from the DEM, the research area was delineated into twenty sub-catchments using ArcHydro toolset in ArcGIS (Figure 2a). Because water quality in the downstream stations was affected by human activities in the upstream catchment, the whole upstream sub-catchments should be taken into consideration when analyzing the downstream monitoring stations.

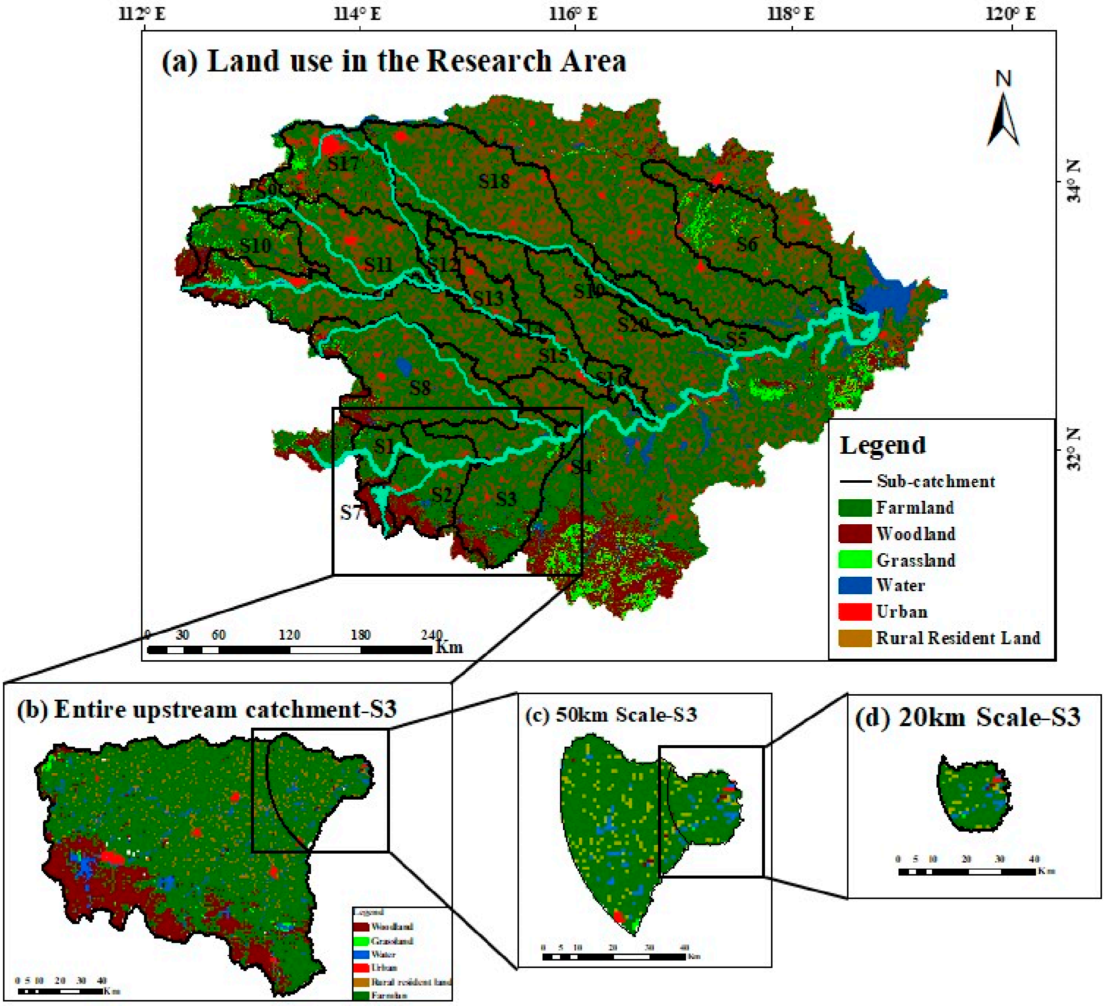

Figure 2. (**a**) The map shows the upper and middle reaches of the Huaihe River Basin. The different colors represent different types of land use. The examples of spatial scales definitions were shown by (**b**) the entire upstream catchment (EUC), (**c**) 50 km radii around the monitor station and (**d**) 20 km radii around the monitor station. The definitions of 10, 15, 30 and 40 km radii scales were similar.

To find out the spatial scales in which the human activities (land use and sewage outfalls) have the most significant impacts on COD and BOD pollution, seven spatial scales were considered in the paper. The local spatial scales of each monitor station were defined as the overlapping area of 10, 15, 20, 30, 40 and 50 km radii around the station location and the corresponding sub-catchment. The catchment-scale was defined as the entire upstream catchment (EUC) of each station [18,20]. The example of EUC, 50 km and 20 km spatial scales are shown in Figure 2b–d, respectively. Six types of land use were included in the study, including farmland (FL), grassland (GL), rural resident land (RRL), urban (UR), water (WA) and woodland (WL) (Figure 2a). The detailed inclusions in each land use type are shown in Table 2.

Table 2. Detailed inclusions of land use types in the study.

Land Use Type	Inclusions
Farmland	Irrigated farmland Dry farmland
Grassland	More than 50% coverage of natural or improved grass 20–50% coverage of natural or improved grass 5–20% coverage of natural or improved grass
Rural resident land	Rural residence
Urban	Built-up area for cities and counties
Water	Rivers Lakes Wetlands Marshes
Woodland	Forests Shrubs Sparsely woodlands

The percentages of the six land use types had no significant change over the research periods (Table 3), besides, land use maps were available only in 2000, 2005 and 2010. Therefore, the dataset from 2000 to 2003, from 2004 to 2008 and from 2009 to 2013 were matched by land use maps in 2000, 2005 and 2010, respectively. Areas of the six land use types and the total amounts of contaminants (COD and BOD) from sewage outfalls were calculated in the seven spatial scales [54]. The datasets in the paper were collected from different sources, which had different physical units and large variations in magnitudes. Therefore, all datasets were scaled following the standardized method before inputting into the models [55].

Table 3. The proportion of the six land use types in 2000, 2005 and 2010 in seven spatial scales.

2000						
Spatial Scale	**FL (%)**	**GL (%)**	**RRL (%)**	**UR (%)**	**WA (%)**	**WL (%)**
10 km	74.47	1.29	14.10	1.93	3.06	5.15
15 km	74.37	1.56	13.25	1.29	3.63	5.90
20 km	74.96	1.32	12.27	0.96	3.68	6.81
30 km	75.62	1.17	12.62	0.94	2.97	6.68
40 km	75.18	1.45	12.60	1.17	2.75	6.85
50 km	75.51	1.36	12.38	1.18	2.59	6.98
EUC	72.50	2.34	10.87	1.60	1.99	10.70
2005						
Spatial Scale	**FL (%)**	**GL (%)**	**RRL (%)**	**UR (%)**	**WA (%)**	**WL (%)**
10 km	73.85	1.29	14.10	2.21	3.40	5.15
15 km	73.81	1.51	13.25	1.49	4.04	5.90
20 km	74.56	1.28	12.28	1.10	3.97	6.81
30 km	75.34	1.14	12.65	1.03	3.16	6.68
40 km	74.81	1.43	12.63	1.37	2.90	6.86
50 km	75.10	1.34	12.41	1.45	2.71	6.99
EUC	71.94	2.33	10.86	2.07	2.13	10.67
2010						
Spatial Scale	**FL (%)**	**GL (%)**	**RRL (%)**	**UR (%)**	**WA (%)**	**WL (%)**
10 km	73.68	1.29	14.03	2.45	3.40	5.15
15 km	73.65	1.51	13.24	1.66	4.04	5.90
20 km	74.32	1.28	12.39	1.23	3.97	6.81
30 km	75.15	1.14	12.70	1.17	3.16	6.68
40 km	75.43	1.47	12.73	1.51	2.96	5.90
50 km	74.93	1.34	12.43	1.59	2.72	6.99
EUC	71.67	2.33	10.88	2.26	2.15	10.71

2.3. Methods

The BN is a graphical method, in which the continuous or discrete variables were represented by nodes and the conditional probability distributions were shown by arrows between nodes. The DAG is used to demonstrate the structure of the BN model, in which the model probability distribution was factorized into local conditional probability distributions of each variable by the Markov property algorithm [34]. Thus, the complex interdependencies can be described in a simple way, accordingly, each variable only depends on its direct parent variables. The BN model works in a two-step way. First, it learns the model structure following the structure learning algorithms. Second, based on conditional dependencies between variables, it estimates the conditional coefficients and conditional probabilities for continuous variables and discrete variables, respectively. Thus, each variable could be analyzed without knowing the precise information about global model distribution [6,36,37].

In the study, the BN was developed to model the complex processes between human activities (land use and sewage outfalls) and oxygen-consuming organic matter indicators (COD and BOD) in dry and wet seasons in the HRB (Figure 3). The six land use types, season scenarios and sewage outfalls were factors that affected COD and BOD at the seven spatial scales. The natural logarithm transformation was undergone on the two water quality indicators to ensure the datasets conform to the Gaussian distribution. The data of water quality indicators, proportions of land use types and amounts of contaminants from sewage outfalls were fed into the BN as continuous data, while season scenarios were inputted as discrete data, namely, "dry season" and "wet season", respectively. Based on the seven spatial scales considered, the spatial data were extracted in all spatial scales, including six land use proportions and amounts of contaminants from sewage outfalls. These data, together with the datasets of water quality indicators, were input into the BN models to find out the spatial scales in which the human activities had the most significant impacts on water quality. The BN model was developed by the "bnlearn" package [56] in the R statistical computing software [57], which is commonly used to do statistical analysis.

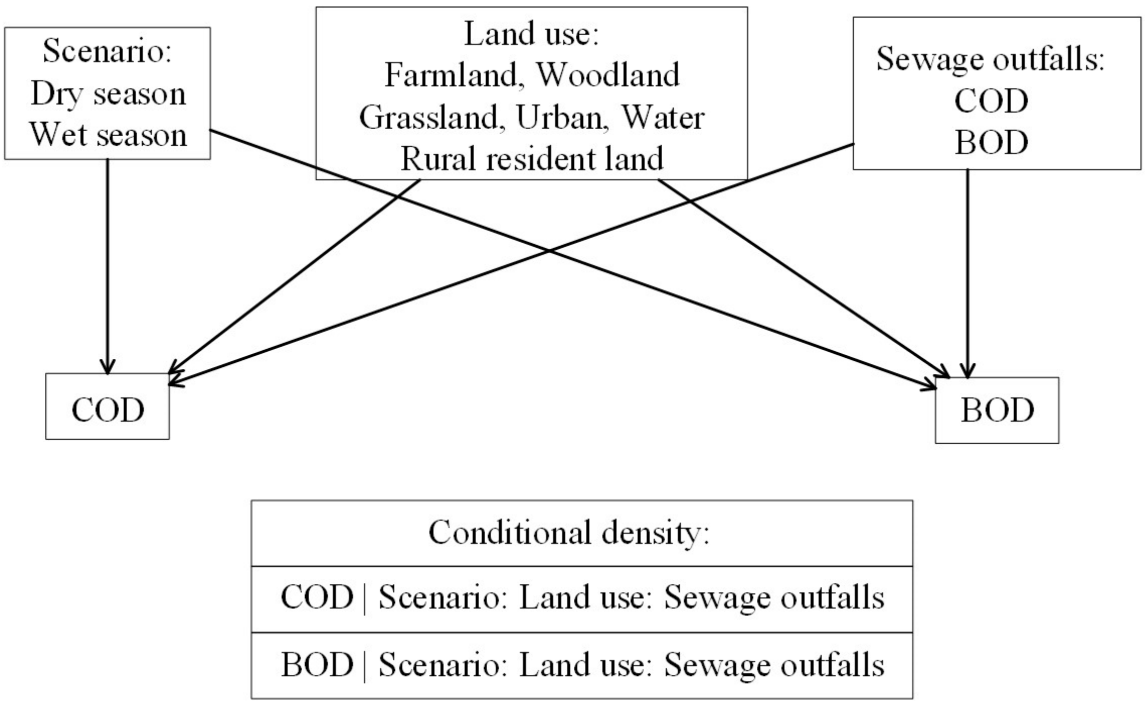

Figure 3. The Bayesian network (BN) structure, which describes chemical oxygen demand (COD) and biochemical oxygen demand (BOD) by season scenarios, percentage of land use types and amounts of contaminants from sewage outfalls in the HRB.

The goodness-of-fit of the BN models were evaluated by Pearson's correlation coefficients (Cor) (Equation (1)) and Nash–Sutcliffe efficiency coefficients (NSE) (Equation (2)) [58,59]. Based on the recommendation by Moriasi, et al. [60], the model can be viewed to be satisfactory with an NSE higher than 0.5. The spatial scales at which human activities had the most significant effects could be determined when the Cor and NSE coefficients obtain the largest values.

$$\mathrm{Cor} = \frac{\sum_{i=1}^{N}\left[\left(obs_i - \overline{pred}\right) \times \left(pred_i - \overline{pred}\right)\right]}{\sqrt{\sum_{i=1}^{N}\left(obs_i - \overline{obs}\right)^2} \times \sqrt{\sum_{i=1}^{N}\left(pred_i - \overline{pred}\right)^2}} \tag{1}$$

$$\mathrm{NSE} = 1 - \frac{\sum_{i=1}^{N}\left(obs_i - pred_i\right)^2}{\sum_{i=1}^{N}\left(obs_i - \overline{obs}\right)^2} \tag{2}$$

where N is the length of dataset; obs_i and $pred_i$ are the values of ith observed and predicted points; $\overline{obs}$ and $\overline{pred}$ are the average values of observed and predicted points.

In order to properly evaluate the influence of land use and sewage outfalls, the contribution of influence factors was calculated based on the predicted parameters from the BN models (Equation (3)).

$$Contribution_i = \frac{Parm_i}{\sum\limits_{i=1}^{n}\left|Parm_i\right|} \times 100\% \tag{3}$$

where $Parm_i$ is the predicted parameter of ith influence factor in the model. The numeric value of *Contribution* presents the magnitude of influence levels while the plus–minus sign represents the positive or negative relationship between the influence factors and the two oxygen-consuming organic matter indicators.

3. Results

3.1. Variations of COD and BOD in Different Seasons

The two oxygen-consuming organic matter indicators had variations in dry and wet seasons in the HRB (Table 4). The mean loads' values of both COD and BOD at all monitor stations were larger in wet seasons than in dry seasons. Accordingly, average COD loads in wet seasons were 2.1 times higher than loads in dry seasons, while the mean loads of BOD in wet seasons were 2.4 times higher than that in dry seasons. The standard deviation of COD in wet seasons was 1.9 times larger than that in dry seasons, while the standard deviation of BOD in wet seasons was 2.7 times higher than in dry seasons.

Table 4. Summary of COD and BOD loads in different seasons at each monitor station in the HRB.

Station Code	COD_Dry (g/s)	COD_Wet (g/s)	BOD_Dry (g/s)	BOD_Wet (g/s)
S1	155 ± 124	905 ± 998	24 ± 15	84 ± 51
S2	433 ± 194	1397 ± 911	62 ± 19	215 ± 105
S3	1272 ± 903	3674 ± 2723	174 ± 186	441 ± 424
S4	2731 ± 2734	5842 ± 4436	314 ± 332	566 ± 594
S5	8253 ± 6129	17548 ± 12744	1585 ± 1715	3527 ± 4447
S6	7871 ± 7303	18935 ± 12492	840 ± 822	2019 ± 2138
S7	18 ± 6	35 ± 61	3 ± 1	11 ± 9
S8	830 ± 509	2514 ± 2175	155 ± 83	372 ± 300
S9	39 ± 31	54 ± 66	12 ± 8	31 ± 39
S10	157 ± 96	185 ± 106	18 ± 11	29 ± 12
S11	370 ± 191	549 ± 139	166 ± 138	215 ± 93
S12	2861 ± 3395	4109 ± 2797	261 ± 235	726 ± 611
S13	4005 ± 4490	6580 ± 6601	748 ± 589	1907 ± 1936
S14	2523 ± 2208	5507 ± 6877	380 ± 403	948 ± 986
S15	3072 ± 2117	6965 ± 6903	408 ± 358	1179 ± 1194
S16	2926 ± 1974	5895 ± 3581	372 ± 402	759 ± 692
S17	645 ± 235	707 ± 247	101 ± 56	127 ± 68
S18	456 ± 375	718 ± 432	53 ± 94	63 ± 77
S19	827 ± 609	1713 ± 1389	111 ± 114	255 ± 267
S20	1827 ± 2388	4133 ± 4660	204 ± 219	908 ± 1570

The lowest COD and BOD were observed at S7, which is the station in tributary at the upper reaches of the HRB (Figure 2b). Water quality indicators at S1 to S4 in upstream of the MRHR were relatively lower than that at S5 and S6 in the downstream of the MRHR. Similarly, water quality at the upstream stations was better than that at the downstream stations in the SYR and GR. As almost all tributaries flowing into the MRHR before the location of S5 and S6, loads of COD and BOD in the area reached the largest values among all monitor stations in the HRB.

3.2. Performances of BN Models at Different Spatial Scales

The spatial scales in which anthropogenic activities had the most significant impacts on water quality were selected by the developed BN models which had the best performance between observations and predictions. The Cor and NSE coefficients were used to evaluate model performance (Figure 4). For COD, the goodness-of-fit of models had a huge increase from the 10 to 15 km scales and then stayed relatively stable. When the analyzed scale reached the EUC, the coefficients reached their maximum. For BOD, the Cor coefficient rose continuously from the 10 to EUC scales, while the NSE coefficient started a significant increase at the 40 km scale. Both Cor and NSE obtained their largest values at the EUC scale for BOD, which is consistent with the result from the COD analysis. Accordingly, the land use and contaminants from sewage outfall in the whole catchment scale (EUC) can give the best explanations for different patterns of COD and BOD. Thus, all analyses about anthropogenic impacts in the research were focused on the EUC scale.

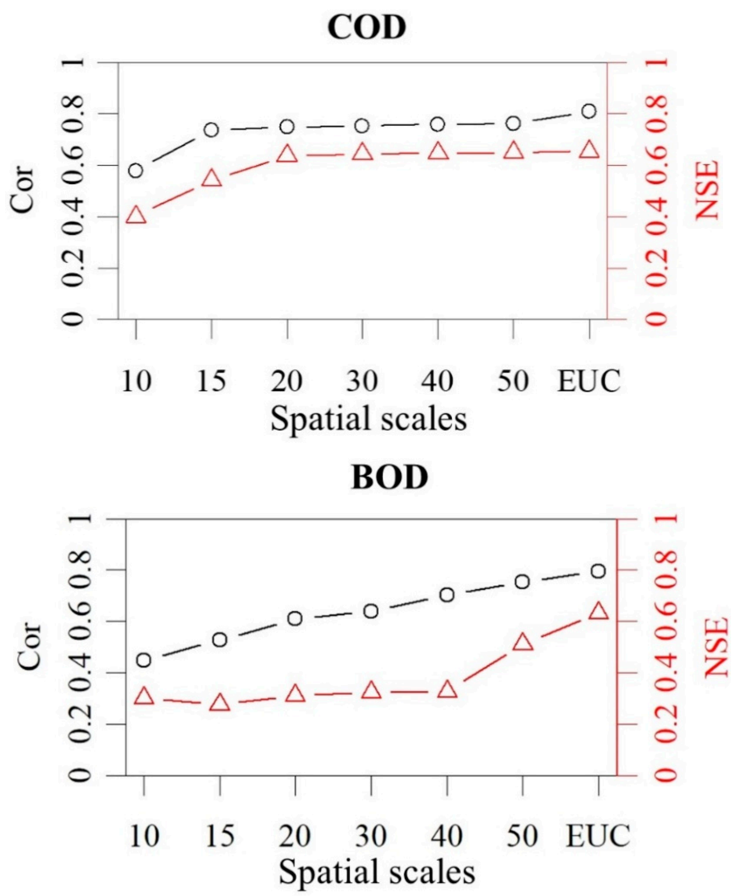

Figure 4. The evaluations of Bayesian networks (BNs) in seven spatial scales by Pearson's correlation coefficients (Cor) and Nash–Sutcliffe efficiency coefficients (NSE). The black and red lines are Cor and NSE, respectively.

The observed values of water quality indicators and predicted values from the BN model in the EUC scales are shown in Figure 5. If the scatter dots spread exactly along the diagonals (red lines), it means that the predictions from models were the same as observed values. Therefore, the model performances for COD (Cor = 0.81, NSE = 0.65) and BOD (Cor = 0.79, NSE = 0.63) in the EUC scale are satisfactory.

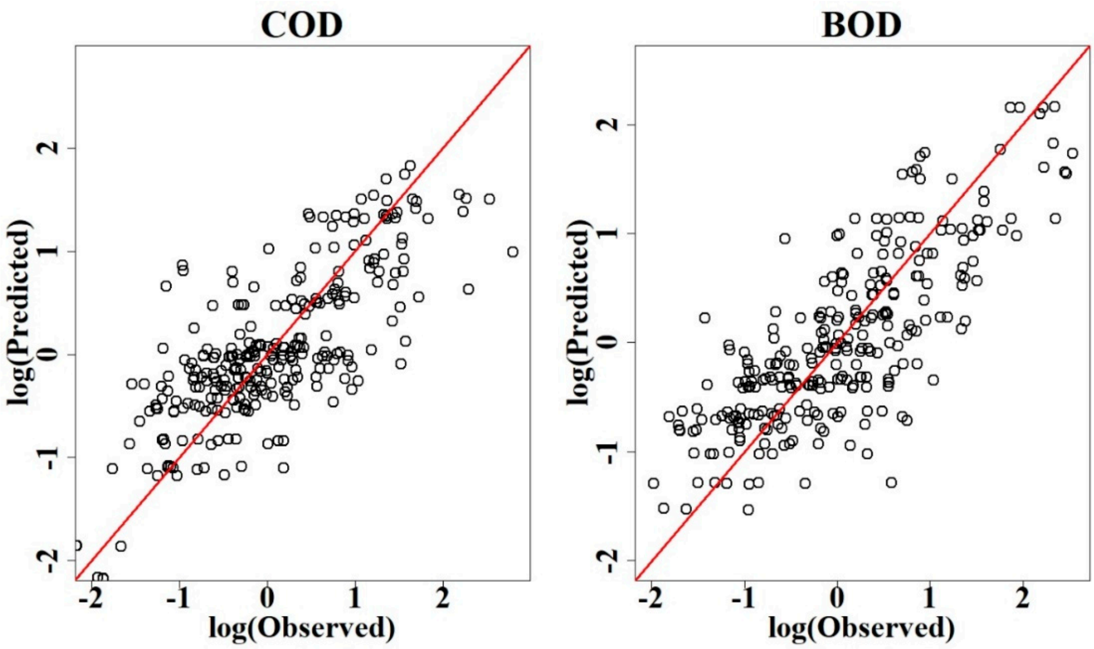

Figure 5. Observed against predicted COD and BOD from BN models at the EUC scale.

3.3. Assessment of Anthropogenic Impacts on COD and BOD in Different Seasons

The parameters of all factors in the EUC scale for dry and wet seasons were shown in Table 5. For COD, the effects of contaminants from sewage outfalls were both positive, which increased COD pollution in two seasons. Considering the farmland and grassland, the effects on COD were negative in dry seasons and became positive in wet seasons. Meanwhile, the woodland had a similar relationship to COD when the scenarios transformed from dry seasons to wet seasons. The correlations between rural residential land and urban land were always positive. The influence of water changed from positive in dry seasons to negative in wet seasons.

Table 5. Parameters of influence factors on COD and BOD from BN models at the EUC scale.

	COD_Dry	COD_Wet	BOD_Dry	BOD_Wet
Sewage outfalls	0.265	0.068	0.244	0.248
FL	−0.195	0.919	−1.137	2.524
GL	−0.191	0.021	−0.712	1.141
RRL	0.076	0.486	−0.139	1.565
UR	0.331	0.483	−0.133	1.444
WA	0.007	−0.069	−0.345	−0.037
WL	−0.103	0.349	−0.975	2.251

The contaminants from sewage outfall had a similar positive influence on BOD. The negative and positive transformation of farmland, grassland and woodland were also implied by the parameters from the BN model. However, the other types of land use (rural residential land, urban and water) had the inverse impacts on BOD in dry seasons when comparing to the impacts on COD. The influence of all factors became positive in wet seasons except the water area.

Based on all parameters predicted from the BN models (Table 5) and Equation (3), the contribution of anthropogenic impacts on water quality could be calculated (Figure 6). In dry seasons, sewage outfalls had significant positive contributions (22.7%) to COD loads, which decreased sharply (2.8%) in wet seasons. The negative contribution of farmland (−16.7%) was in a similar magnitude to grassland (−16.4%) in dry seasons. When comes to wet seasons, farmland became the biggest positive contribution (38.4%) to COD. Thus, the “sink” and “source” processes of farmland depends on different seasons.

The grassland and woodland also had similar patterns that changed from "sink" in dry seasons to "source" in wet seasons, although the positive influence of grassland (0.9%) was very weak. The rural residential land and urban land worked as pollution sources for COD in both seasons. The contribution of the former one had a huge increase (from 6.5% to 20.3%) in wet seasons while the latter one decreased a little (from 28.3% to 20.2%) at the same time. Besides, results suggested that the water area showed no significant influence on COD, specifically, the contribution was 0.6% in dry seasons and −2.9% in wet seasons. In general, the sewage outfalls and urban land had the most significant positive effects on COD in dry seasons while the farmland had significant contributions to COD pollution in wet seasons.

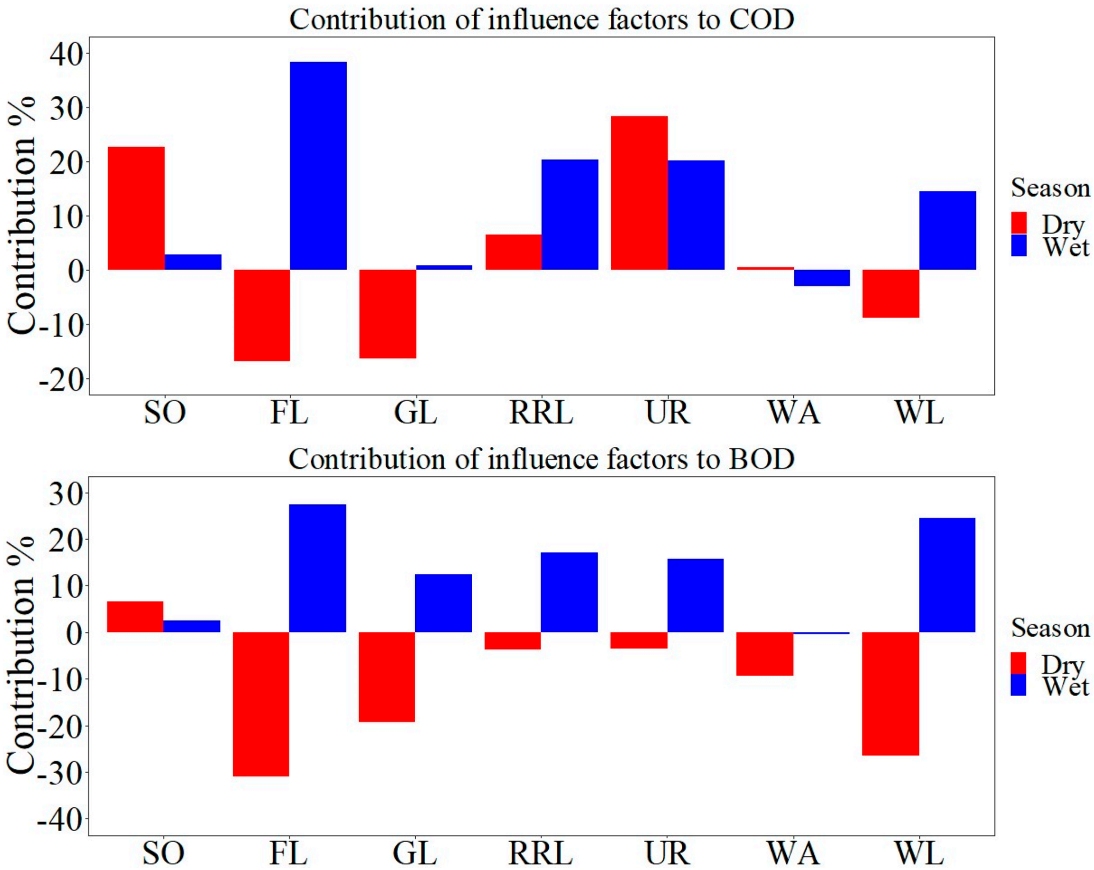

Figure 6. Contribution of influence factors to COD and BOD in dry and wet seasons. The SO, FL, GL, RRL, UR, WA and WL are sewage outfalls, farmland, grassland, rural residential land, urban, water and woodland, respectively.

The positive contribution of sewage outfalls to BOD was less than that of COD, which was 6.6% in dry seasons and 2.7% in wet seasons. The farmland, grassland and woodland had significant negative effects on BOD in dry seasons and the contributions were −30.9%, −19.3% and −26.5% respectively. However, the farmland (27.4%) and woodland (24.4%) both became the strongest positive contributors to BOD in wet seasons. The rural residential land and urban land were the second-largest contributors to BOD pollution, which was 16.9% and 15.8%, contribution respectively. The positive relationship between water and BOD was negligible.

4. Discussion

The research implied that anthropogenic activities had the most significant impacts on the oxygen-consuming organic matter indicators (COD and BOD) at the EUC scale in the HRB. It was consistent with previous research that focused on other river basins, such as the Dongjiang River basin in China, the Adour-Garonne basin in southwestern France and the Córrego Água Limpa in

Brazil [16,19,61]. However, some studies suggested that the land use in relative finer scales had more effects on water quality [62,63]. One possible reason was that the local scales were delineated by different methods, which induced different areas of land use types [19]. Besides, different water quality parameters tend to have different dominant spatial scales. For example, based on our previous research, the most significant spatial scale for ammonia nitrogen (AN) and dissolved oxygen (DO) in the HRB was the local scales within 20 km radii around monitor stations [53]. It was caused by the various chemical properties of these water contaminants. As a result of long water residence time in the HRB, the nitrification and denitrification processes were intensive in groundwater adjacent to the riparian zone [64]. Thus, nutrients contaminants were more significantly correlated to land use at local scales. Besides, for DO, given a certain contact time, the reoxygenation processes could reach oxygen equilibrium again in the water body under normal conditions. In this way, the contaminants transporting from long distances would not play an important role in determining the DO levels in rivers. However, COD and BOD, which are indicators of oxygen-consuming organic matters, are relatively stable, thus the degradation of organic compounds needs more time. Moreover, studies found that COD was positive correlated with sediment levels, which means that sediment particles could work as carriers of COD contaminants from land to rivers by flush processes across the catchment scale [61,65,66]. Therefore, the human activities in the whole catchment scale played the most important role in organic pollution in water body.

The percentage of different land use types are various from local to catchment scales. Besides, the total amount of contaminants discharged from sewage outfalls also has huge differences across the seven spatial scales (Table 6), which were about 30 times higher in the EUC scale than those in the 10 km radii scale. It is the main reason why human activities in the catchment scale could give the best explanation to variations of COD and BOD in the HRB. The results suggested that efficient strategies for better water environment protection should consider different spatial scales based on different characteristics of contaminants matters. Accordingly, for unstable water quality indicators, more attention should be paid in local scales around monitor stations, while for stable contaminants, management on the whole catchments should be implemented.

Table 6. The total amount of COD and BOD from sewage outfalls in seven spatial scales over the research period.

Spatial Scale	COD (Ton/Year)	BOD (Ton/Year)
10 km	203.3	49.9
15 km	243.5	57.7
20 km	301.6	75.6
30 km	488.2	121.0
40 km	720.1	199.8
50 km	1072.6	315.2
EUC	5329.4	1555.7

Impacts of human activities on water quality include two parts: point sources of contaminants emitted from domestic or industrial outfalls and nonpoint sources transported by soil erosion and surface runoff from lands [67]. As contaminants from point sources had no necessary correlation to land use types, taking the influence of sewage outfalls into consideration helps to improve the assessments of human impacts on the water environment [68]. Based on previous results, the contribution of point sources to COD and BOD have overwhelmed the contribution of nonpoint sources, which highlights the importance of sufficient wastewater treatments in improving water quality in river basins [69–71]. In our research, the contaminants from sewage outfalls were main contributors to water pollution, especially in dry seasons. Since controlling contaminants from sewage outfalls could be easier than controlling contaminants from nonpoint sources, for example, from farmlands or urban areas, attention should be paid to increasing the percentage of treated wastewater. Because the amounts of wastewater were emitted from sewage outfalls continuously and stably under normal conditions in the HRB, their contribution were decreased because of dilution by the increasing discharge in wet seasons.

Farmland is the main influence factor of COD and BOD, which works as a "sink" for organic pollution in dry seasons and "source" in wet seasons. Similar patterns had been observed by our previous study, which focused on nutrients and DO in this area [53]. One potential reason is that the surface runoff in the HRB had huge variations between dry and wet seasons (Table 7). Based on the T-test, discharge values had a significant difference, accordingly, three times higher in wet seasons than that in dry seasons. As organic matters from farmland were transported by sediment particles [61,65,66], the organic contaminants possibly could not be moved to receiving water and therefore were stored in farmland due to lacking enough surface runoff in dry seasons. When wet seasons occurred, increased surface runoff caused soil erosion and sediment transportation. The larger transportation capacity carried more pollution into rivers, including contaminates reserved in the former dry season and produced by agricultural activities in the current wet seasons. The transformed "sink" and "source" processes in farmland were a potential reason for the phenomenon that COD and BOD loads were both higher in wet seasons than those in dry seasons, which was similar to several previous studies [29,72,73]. Since the farmland had the largest proportion in the HRB and played an important role in water degradation, it is urgent to take measures to reduce organic matters transported from farmland, such as controlling the use of agricultural fertilizers, establishing a "field–ditch–pond" structure and constructing wetland detention ponds near riparian areas [65,74,75].

Table 7. The T-test of discharge in different seasons at all monitor stations in the HRB.

Station Code	Dry (m^3/s)	Wet (m^3/s)	p Value
S1	12.04 ± 34.39	49.83 ± 157.43	$<2 \times 10^{-16}$
S2	49.50 ± 94.22	161.72 ± 385.20	$<2 \times 10^{-16}$
S3	70.95 ± 99.03	238.82 ± 498.41	$<2 \times 10^{-16}$
S4	127.94 ± 178.16	343.16 ± 510.42	$<2 \times 10^{-16}$
S5	423.33 ± 469.93	1223.20 ± 1587.28	$<2 \times 10^{-16}$
S6	453.25 ± 527.52	1250.87 ± 1661.13	$<2 \times 10^{-16}$
S7	1.15 ± 3.23	3.77 ± 16.17	4×10^{-12}
S8	32.73 ± 77.31	103.82 ± 249.90	$<2 \times 10^{-16}$
S9	1.76 ± 3.57	3.45 ± 5.37	$<2 \times 10^{-16}$
S10	7.93 ± 11.38	15.43 ± 14.40	4×10^{-16}
S11	24.76 ± 27.78	35.38 ± 56.68	1×10^{-8}
S12	67.97 ± 93.69	130.52 ± 280.72	$<2 \times 10^{-16}$
S13	83.35 ± 105.03	159.65 ± 313.23	$<2 \times 10^{-16}$
S14	84.50 ± 111.88	171.39 ± 327.40	$<2 \times 10^{-16}$
S15	114.37 ± 146.15	244.21 ± 396.42	$<2 \times 10^{-16}$
S16	109.92 ± 133.53	209.07 ± 354.49	$<2 \times 10^{-16}$
S17	7.47 ± 11.08	20.18 ± 15.06	$<2 \times 10^{-16}$
S18	21.69 ± 14.81	34.78 ± 43.70	$<2 \times 10^{-16}$
S19	26.70 ± 34.70	51.29 ± 113.30	$<2 \times 10^{-16}$
S20	52.87 ± 61.73	119.02 ± 201.65	$<2 \times 10^{-16}$

Grassland and woodland had significant negative effects on COD and BOD in dry seasons which could work as a pollution buffer around rivers. It was because that denser vegetation could reduce runoff volumes and intercept contaminants [76–79]. Therefore, woodland and grassland could have better water and soil conservation functions to reduce water pollution from nonpoint sources [80–84]. However, the woodland became a source of organic contaminants in wet seasons due to largely increased surface runoff.

Urban had a significant positive contribution to COD in both seasons, which was related to the high percentage of impervious surface coverage in the area. Without the infiltration process happening on the soil surface, the overland runoff on the impervious ground could be generated under even slight rainfalls in dry seasons. Therefore, the contributions of urban areas were insensitive to the variations of the surface runoff between dry and wet seasons when comparing to farmland's soil surface, which experienced the transition between the "sink" and "source" processes. Although urban areas had a slightly weak negative contribution to BOD in dry seasons, it became a fundamental source of BOD contaminants in wet seasons. In general, the urban areas made significant contributions to increasing the organic pollution in the HRB. The results were consistent with previous studies, which highlighted that intensive anthropogenic activities, such as food waste, stocked garbage and domestic wastewater, played an important role in water quality degradations [13,37,52,85].

5. Conclusions

To assess anthropogenic impacts on COD and BOD in dry and wet seasons in the HRB, the BNs were applied to model the complex processes. The most significant effects of land use and sewage outfalls on COD and BOD were at the catchment scale. Key results are as follows:

(1) The sewage outfalls played an important role in organic pollution in dry seasons, while farmland became the most important source in wet seasons although it showed the "sink" process in dry seasons.
(2) Intensive human activities in urban areas always played an important role in increasing COD levels in the HRB.
(3) Grassland had a negative relationship to organic pollution, especially in dry seasons, thus it could be used as a river buffer based on its capacity to intercept and retain contaminants.

The results highlight the significance of comprehensively considering different spatial scales in assessing the anthropogenic impacts on water degradation, especially for different water indicators. In order to better improve water quality in the HRB, more attention should be paid by governments to controlling organic matters transported from farmland and urban to the waterbody. Increasing the efficiency of wastewater treatments and the percentage of grassland in the riparian zone could help to protect the water environment. For comprehensive assessments of the influence factors on the water environment, the BN model could provide a convenient way to model complex processes in river systems, which could be applied not only in the HRB, but also in other river basins over the world.

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References

1. Santos, R.M.B.; Sanches Fernandes, L.F.; Pereira, M.G.; Cortes, R.M.V.; Pacheco, F.A.L. A framework model for investigating the export of phosphorus to surface waters in forested watersheds: Implications to management. *Sci. Total Environ.* **2015**, *536*, 295–305. [CrossRef] [PubMed]
2. Hollaway, M.J.; Beven, K.J.; Benskin, C.M.H.; Collins, A.L.; Evans, R.; Falloon, P.D.; Forber, K.J.; Hiscock, K.M.; Kahana, R.; Macleod, C.J.A.; et al. The challenges of modelling phosphorus in a headwater catchment: Applying a 'limits of acceptability' uncertainty framework to a water quality model. *J. Hydrol.* **2018**, *558*, 607–624. [CrossRef]

3. Williams, M.R.; King, K.W.; Macrae, M.L.; Ford, W.; Van Esbroeck, C.; Brunke, R.I.; English, M.C.; Schiff, S.L. Uncertainty in nutrient loads from tile-drained landscapes: Effect of sampling frequency, calculation algorithm, and compositing strategy. *J. Hydrol.* **2015**, *530*, 306–316. [CrossRef]
4. Wang, R.; Xu, T.; Yu, L.; Zhu, J.; Li, X. Effects of land use types on surface water quality across an anthropogenic disturbance gradient in the upper reach of the Hun River, Northeast China. *Environ. Monit. Assess.* **2013**, *185*, 4141–4151. [CrossRef]
5. Schindler, D.W.; Carpenter, S.R.; Chapra, S.C.; Hecky, R.E.; Orihel, D.M. Reducing Phosphorus to Curb Lake Eutrophication is a Success. *Environ. Sci. Technol.* **2016**, *50*, 8923–8929. [CrossRef]
6. Couture, R.-M.; Moe, S.J.; Lin, Y.; Kaste, Ø.; Haande, S.; Lyche Solheim, A. Simulating water quality and ecological status of Lake Vansjø, Norway, under land-use and climate change by linking process-oriented models with a Bayesian network. *Sci. Total Environ.* **2018**, *621*, 713–724. [CrossRef]
7. Selle, B.; Schwientek, M.; Lischeid, G. Understanding processes governing water quality in catchments using principal component scores. *J. Hydrol.* **2013**, *486*, 31–38. [CrossRef]
8. Carey, R.O.; Hochmuth, G.J.; Martinez, C.J.; Boyer, T.H.; Dukes, M.D.; Toor, G.S.; Cisar, J.L. Evaluating nutrient impacts in urban watersheds: Challenges and research opportunities. *Environ. Pollut.* **2013**, *173*, 138–149. [CrossRef]
9. Elçi, Ş.; Selçuk, P. Effects of basin activities and land use on water quality trends in Tahtali Basin, Turkey. *Environ. Earth Sci.* **2013**, *68*, 1591–1598. [CrossRef]
10. Gao, X.; Niu, C.; Chen, Y.; Yin, X. Spatial heterogeneity of stream environmental conditions and macroinvertebrates community in an agriculture dominated watershed and management implications for a large river (the Liao River, China) basin. *Environ. Monit. Assess.* **2014**, *186*, 2375–2391. [CrossRef]
11. Liu, J.; Zhang, X.; Wu, B.; Pan, G.; Xu, J.; Wu, S. Spatial scale and seasonal dependence of land use impacts on riverine water quality in the Huai River basin, China. *Environ. Sci. Pollut. Res.* **2017**, *24*, 20995–21010. [CrossRef] [PubMed]
12. Julian, J.P.; Beurs, K.M.D.; Owsley, B.; Davies-Colley, R.J.; Ausseil, A.G.E. River water quality changes in New Zealand over 26 years (1989–2014): Response to land use and land disturbance. *Hydrol. Earth Syst. Sci. Discuss.* **2016**, *21*, 1–69.
13. Meneses, B.M.; Reis, R.; Vale, M.J.; Saraiva, R. Land use and land cover changes in Zêzere watershed (Portugal)—Water quality implications. *Sci. Total Environ.* **2015**, *527*, 439–447. [CrossRef] [PubMed]
14. Keesstra, S.D.; Temme, A.J.A.M.; Schoorl, J.M.; Visser, S.M. Evaluating the hydrological component of the new catchment-scale sediment delivery model LAPSUS-D. *Geomorphology* **2014**, *212*, 97–107. [CrossRef]
15. Vrebos, D.; Beauchard, O.; Meire, P. The impact of land use and spatial mediated processes on the water quality in a river system. *Sci. Total Environ.* **2017**, *601*, 365–373. [CrossRef] [PubMed]
16. Tudesque, L.; Tisseuil, C.; Lek, S. Scale-dependent effects of land cover on water physico-chemistry and diatom-based metrics in a major river system, the Adour-Garonne basin (South Western France). *Sci. Total Environ.* **2014**, *466*, 47–55. [CrossRef]
17. Wang, G.; Xu, Z.; Zhang, S. The influence of land use patterns on water quality at multiple spatial scales in a river system. *Hydrol. Process.* **2015**, *28*, 5259–5272. [CrossRef]
18. Hurley, T.; Mazumder, A. Spatial scale of land-use impacts on riverine drinking source water quality. *Water Resour. Res.* **2013**, *49*, 1591–1601. [CrossRef]
19. Ding, J.; Jiang, Y.; Liu, Q.; Hou, Z.; Liao, J.; Fu, L.; Peng, Q. Influences of the land use pattern on water quality in low-order streams of the Dongjiang River basin, China: A multi-scale analysis. *Sci. Total Environ.* **2016**, *551*, 205–216. [CrossRef]
20. Delpla, I.; Rodriguez, M.J. Effects of future climate and land use scenarios on riverine source water quality. *Sci. Total Environ.* **2014**, *493*, 1014–1024. [CrossRef]
21. Chang, H. Spatial analysis of water quality trends in the Han River basin, South Korea. *Water Res.* **2008**, *42*, 3285–3304. [CrossRef] [PubMed]
22. Seeboonruang, U. A statistical assessment of the impact of land uses on surface water quality indexes. *J. Environ. Manag.* **2012**, *101*, 134–142. [CrossRef] [PubMed]
23. Wang, J.-Z.; Chen, T.-H.; Zhu, C.-Z.; Peng, S.-C. Trace organic pollutants in sediments from Huaihe River, China: Evaluation of sources and ecological risk. *J. Hydrol.* **2014**, *512*, 463–469. [CrossRef]
24. Bu, H.; Wei, M.; Yuan, Z.; Wan, J. Relationships between land use patterns and water quality in the Taizi River basin, China. *Ecol. Indic.* **2014**, *41*, 187–197. [CrossRef]

25. Xu, J.; Jin, G.; Tang, H.; Zhang, P.; Wang, S.; Wang, Y.-G.; Li, L. Assessing temporal variations of Ammonia Nitrogen concentrations and loads in the Huaihe River Basin in relation to policies on pollution source control. *Sci. Total Environ.* **2018**, *642*, 1386–1395. [CrossRef]
26. Zhai, X.; Xia, J.; Zhang, Y. Integrated approach of hydrological and water quality dynamic simulation for anthropogenic disturbance assessment in the Huai River Basin, China. *Sci. Total Environ.* **2017**, *598*, 749–764. [CrossRef]
27. Zhao, C.; Liu, C.; Xia, J.; Zhang, Y.; Yu, Q.; Eamus, D. Recognition of key regions for restoration of phytoplankton communities in the Huai River basin, China. *J. Hydrol.* **2012**, *420*, 292–300. [CrossRef]
28. *Water Pollution Prevention and Control Plan for the Huai River Basin*; Ministry of Environmental Protection of the People Republic of China: Beijing, China, 1996.
29. Xu, G.; Ren, X.; Yang, Z.; Long, H.; Xiao, J. Influence of Landscape Structures on Water Quality at Multiple Temporal and Spatial Scales: A Case Study of Wujiang River Watershed in Guizhou. *Water* **2019**, *11*, 159. [CrossRef]
30. Hwang, S.-A.; Hwang, S.-J.; Park, S.-R.; Lee, S.-W. Examining the Relationships between Watershed Urban Land Use and Stream Water Quality Using Linear and Generalized Additive Models. *Water* **2016**, *8*, 155. [CrossRef]
31. Yuan, D.; Liu, Y.; Guo, X.; Liu, J. Characteristic contaminants in snowpack and snowmelt surface runoff from different functional areas in Beijing, China. *Environ. Sci. Pollut. Res.* **2018**, *25*, 36256–36266. [CrossRef]
32. Zhai, X.; Xia, J.; Zhang, Y. Water quality variation in the highly disturbed Huai River Basin, China from 1994 to 2005 by multi-statistical analyses. *Sci. Total Environ.* **2014**, *496*, 594–606. [CrossRef] [PubMed]
33. Jiang, Y.; Peng, Q.-D.; Luo, H.-H.; Ma, M. Analysis of spatial and temporal variation of water quality in Huiahe River Basin. *J. Hydraul. Eng.* **2011**, *42*, 1283–1288. (In Chinese) [CrossRef]
34. Korb, K.B.; Nicholson, A.E. *Bayesian Artificial Intelligence*; Chapman Hall: Atlanta, GA, USA, 2004.
35. Aguilera, P.A.; Fernández, A.; Fernández, R.; Rumí, R.; Salmerón, A. Bayesian networks in environmental modelling. *Environ. Model. Softw.* **2011**, *26*, 1376–1388. [CrossRef]
36. Li, Y.; Jia, Z.; Wijesiri, B.; Song, N.; Goonetilleke, A. Influence of traffic on build-up of polycyclic aromatic hydrocarbons on urban road surfaces: A Bayesian network modelling approach. *Environ. Pollut.* **2018**, *237*, 767–774. [CrossRef]
37. Wijesiri, B.; Deilami, K.; Goonetilleke, A. Evaluating the relationship between temporal changes in land use and resulting water quality. *Environ. Pollut.* **2018**, *234*, 480–486. [CrossRef]
38. Sun, R.; Yuan, H.; Liu, X.; Jiang, X. Evaluation of the latest satellite–gauge precipitation products and their hydrologic applications over the Huaihe River basin. *J. Hydrol.* **2016**, *536*, 302–319. [CrossRef]
39. Zhang, R.; Chen, X.; Cheng, Q.; Zhang, Z.; Shi, P. Joint probability of precipitation and reservoir storage for drought estimation in the headwater basin of the Huaihe River, China. *Stoch. Environ. Res. Risk Assess.* **2016**, *30*, 1641–1657. [CrossRef]
40. Cao, Q.; Hao, Z.; Yuan, F.; Berndtsson, R.; Xu, S.; Gao, H.; Hao, J. On the Predictability of Daily Rainfall during Rainy Season over the Huaihe River Basin. *Water* **2019**, *11*, 916. [CrossRef]
41. Yu, Z.-L.; Yan, D.-H.; Ni, G.-H.; Do, P.; Yan, D.-M.; Cai, S.-Y.; Qin, T.-L.; Weng, B.-S.; Yang, M.-J. Variability of Spatially Grid-Distributed Precipitation over the Huaihe River Basin in China. *Water* **2017**, *9*, 489. [CrossRef]
42. *Water Pollution Prevention and Control Plan for the Huai River Basin*; Ministry of Environmental Protection of the People Republic of China: Beijing, China, 2006.
43. *Water Pollution Prevention and Control Plan for the Huai River Basin*; Ministry of Environmental Protection of the People Republic of China: Beijing, China, 2010.
44. Chen, X.; Cao, W.; Wang, X.; Yao, Y.; Yue, W. Analysis of agroclimatic resource characteristics of main crops growing season in the south of Huaihe River Basin. *Ecol. Environ. Sci.* **2018**, *27*, 1005–1015.
45. Zhang, J.; Wang, X. Spatial-temporal Analysis of the Water Surplus Deficit Index for the Summer Corn Key period in the Huaihe Basin. *Chin. Agric. Sci. Bull.* **2014**, *30*, 100–105.
46. Liao, M.; Yan, Y.; Zheng, Q.; Wang, Y.; Wang, Z.; Ma, T. Study on specific vulnerability of nitrate in shallow groundwater in Huaihe River Basin. *J. Nanjing Univ. Nat. Sci.* **2016**, *52*, 86–95.
47. Song, D.; Chen, W.; Gao, Y. The usage rationality and environmental impacts of chemical nitrogen fertilizer and pesticide in the Huaihe River Basin, China. *J. Agro Environ. Sci.* **2011**, *30*, 1144–1151.

48. Wang, J.; Liu, G.; Zhang, J.; Liu, H.; Lam, P.K.S. A 59-year sedimentary record of metal pollution in the sediment core from the Huaihe River, Huainan, Anhui, China. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 1–13. [CrossRef]
49. Meng, J.; Wang, T.; Wang, P.; Giesy, J.P.; Lu, Y. Perfluoroalkyl substances and organochlorine pesticides in sediments from Huaihe watershed in China. *J. Environ. Sci.* **2014**, *26*, 2198–2206. [CrossRef]
50. *Water Quality-Determination of the Chemical Oxygen Demand-Dichromate Method*; Ministry of Environmental Protection of the People's Republic of China: Beijing, China, 1989.
51. *Water Quality-Determination of Biochemical Oxygen Demand after 5 Days (BOD5) for Dilution and Seeding Method*; Ministry of Environmental Protection of the People's Republic of China: Beijing, China, 1987.
52. Chen, Q.; Mei, K.; Dahlgren, R.A.; Wang, T.; Gong, J.; Zhang, M. Impacts of land use and population density on seasonal surface water quality using a modified geographically weighted regression. *Sci. Total Environ.* **2016**, *572*, 450–466. [CrossRef]
53. Xu, J.; Jin, G.; Tang, H.; Mo, Y.; Wang, Y.-G.; Li, L. Response of water quality to land use and sewage outfalls in different seasons. *Sci. Total Environ.* **2019**, *696*, 134014. [CrossRef]
54. Bostanmaneshrad, F.; Partani, S.; Noori, R.; Nachtnebel, H.-P.; Berndtsson, R.; Adamowski, J.F. Relationship between water quality and macro-scale parameters (land use, erosion, geology, and population density) in the Siminehrood River Basin. *Sci. Total Environ.* **2018**, *639*, 1588–1600. [CrossRef]
55. Fijani, E.; Barzegar, R.; Deo, R.; Tziritis, E.; Skordas, K. Design and implementation of a hybrid model based on two-layer decomposition method coupled with extreme learning machines to support real-time environmental monitoring of water quality parameters. *Sci. Total Environ.* **2019**, *648*, 839–853. [CrossRef]
56. Scutari, M. Learning Bayesian Networks with the bnlearn R Package. *J. Stat. Softw.* **2010**, *35*, 2010. [CrossRef]
57. Team, R.C. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2016.
58. Nash, J.E.; Sutcliffe, J.V. River flow forecasting through conceptual models part I—A discussion of principles. *J. Hydrol.* **1970**, *10*, 282–290. [CrossRef]
59. Jang, C.; Kum, D.; Jung, Y.; Kim, K.; Shin, D.S.; Engel, B.A.; Shin, Y.; Lim, K.J. Development of a Web-Based L-THIA 2012 Direct Runoff and Pollutant Auto-Calibration Module Using a Genetic Algorithm. *Water* **2013**, *5*, 1952–1966. [CrossRef]
60. Moriasi, D.N.; Arnold, J.G.; Van Liew, M.W.; Bingner, R.L.; Harmel, R.D.; Veith, T.L. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Trans. ASABE* **2007**, *50*, 885–900. [CrossRef]
61. Rodrigues, V.; Estrany, J.; Ranzini, M.; de Cicco, V.; Martín-Benito, J.M.T.; Hedo, J.; Lucas-Borja, M.E. Effects of land use and seasonality on stream water quality in a small tropical catchment: The headwater of Córrego Água Limpa, São Paulo (Brazil). *Sci. Total Environ.* **2018**, *622*, 1553–1561. [CrossRef] [PubMed]
62. Tran, C.P.; Bode, R.W.; Smith, A.J.; Kleppel, G.S. Land-use proximity as a basis for assessing stream water quality in New York State (USA). *Ecol. Indic.* **2010**, *10*, 727–733. [CrossRef]
63. Dosskey, M.G.; Vidon, P.; Gurwick, N.P.; Allan, C.J.; Duval, T.P.; Lowrance, R. The role of riparian vegetation in protecting and improving chemical water quality in streams. *JAWRA J. Am. Water Resour. Assoc.* **2010**, *46*, 261–277. [CrossRef]
64. Meynendonckx, J.; Heuvelmans, G.; Muys, B.; Feyen, J. Effects of watershed and riparian zone characteristics on nutrient concentrations in the River Scheldt Basin. *Hydrol. Earth Syst. Sci.* **2006**, *3*, 913–922. [CrossRef]
65. Zhao, J.; Zhao, Y.; Zhao, X.; Jiang, C. Agricultural runoff pollution control by a grassed swales coupled with wetland detention ponds system: A case study in Taihu Basin, China. *Environ. Sci. Pollut. Res.* **2016**, *23*, 9093–9104. [CrossRef]
66. Wang, J.; Cheng, Q.; Xue, S.; Rajendran, M.; Wu, C.; Liao, J. Pollution characteristics of surface runoff under different restoration types in manganese tailing wasteland. *Environ. Sci. Pollut. Res.* **2018**, *25*, 9998–10005. [CrossRef]
67. Peng, C.; He, J.-T.; Wang, M.-L.; Zhang, Z.-G.; Wang, L. Identifying and assessing human activity impacts on groundwater quality through hydrogeochemical anomalies and NO_3^-, NH_4^+, and COD contamination: A case study of the Liujiang River Basin, Hebei Province, P.R. China. *Environ. Sci. Pollut. Res.* **2018**, *25*, 3539–3556. [CrossRef]

68. Zhou, P.; Huang, J.; Pontius, R.G.; Hong, H. New insight into the correlations between land use and water quality in a coastal watershed of China: Does point source pollution weaken it? *Sci. Total Environ.* **2016**, *543*, 591–600. [CrossRef] [PubMed]
69. Fučík, P.; Novák, P.; Žížala, D. A combined statistical approach for evaluation of the effects of land use, agricultural and urban activities on stream water chemistry in small tile-drained catchments of south Bohemia, Czech Republic. *Environ. Earth Sci.* **2014**, *72*, 2195–2216. [CrossRef]
70. Shukla, A.K.; Ojha, C.S.P.; Mijic, A.; Buytaert, W.; Pathak, S.; Garg, R.D.; Shukla, S. Population growth, land use and land cover transformations, and water quality nexus in the Upper Ganga River basin. *Hydrol. Earth Syst. Sci.* **2018**, *22*, 4745–4770. [CrossRef]
71. Zhao, W.; Zhu, X.; Sun, X.; Shu, Y.; Li, Y. Water quality changes in response to urban expansion: Spatially varying relations and determinants. *Environ. Sci. Pollut. Res.* **2015**, *22*, 16997–17011. [CrossRef]
72. Yadav, S.; Babel, M.S.; Shrestha, S.; Deb, P. Land use impact on the water quality of large tropical river: Mun River Basin, Thailand. *Environ. Monit. Assess.* **2019**, *191*, 614. [CrossRef]
73. Kim, K.; Kim, B.; Eum, J.; Seo, B.; Shope, C.L.; Peiffer, S. Impacts of Land Use Change and Summer Monsoon on Nutrients and Sediment Exports from an Agricultural Catchment. *Water* **2018**, *10*, 544. [CrossRef]
74. Zhang, Z.-Y.; Kong, L.-L.; Zhu, L.; Xia, J.-H.; Patricia, X. Fate characteristics of nitrogen in runoff from a small agricultural watershed on the south of Huaihe River in China. *Environ. Earth Sci.* **2012**, *66*, 835–848. [CrossRef]
75. Li, R.; Ruan, X.; Bai, Y.; Ma, T.; Liu, C. Effect of wheat-maize straw return on the fate of nitrate in groundwater in the Huaihe River Basin, China. *Sci. Total Environ.* **2017**, *592*, 78–85. [CrossRef]
76. Le Bouteiller, C.; Venditti, J.G. Sediment transport and shear stress partitioning in a vegetated flow. *Water Resour. Res.* **2015**, *51*, 2901–2922. [CrossRef]
77. Kang, S.; Zhang, L.; Song, X.; Zhang, S.; Liu, X.; Liang, Y.; Zheng, S. Runoff and sediment loss responses to rainfall and land use in two agricultural catchments on the Loess Plateau of China. *Hydrol. Process.* **2001**, *15*, 977–988. [CrossRef]
78. Rodriguez-Lloveras, X.; Bussi, G.; Francés, F.; Rodriguez-Caballero, E.; Solé-Benet, A.; Calle, M.; Benito, G. Patterns of runoff and sediment production in response to land-use changes in an ungauged Mediterranean catchment. *J. Hydrol.* **2015**, *531*, 1054–1066. [CrossRef]
79. Gonzales-Inca, C.; Valkama, P.; Lill, J.-O.; Slotte, J.; Hietaharju, E.; Uusitalo, R. Spatial modeling of sediment transfer and identification of sediment sources during snowmelt in an agricultural watershed in boreal climate. *Sci. Total Environ.* **2018**, *612*, 303–312. [CrossRef] [PubMed]
80. Wang, F.; Hessel, R.; Mu, X.; Maroulis, J.; Zhao, G.; Geissen, V.; Ritsema, C. Distinguishing the impacts of human activities and climate variability on runoff and sediment load change based on paired periods with similar weather conditions: A case in the Yan River, China. *J. Hydrol.* **2015**, *527*, 884–893. [CrossRef]
81. Ha, M.; Zhang, Z.; Wu, M. Biomass production in the Lower Mississippi River Basin: Mitigating associated nutrient and sediment discharge to the Gulf of Mexico. *Sci. Total Environ.* **2018**, *635*, 1585–1599. [CrossRef]
82. Uwimana, A.; van Dam, A.A.; Gettel, G.M.; Irvine, K. Effects of agricultural land use on sediment and nutrient retention in valley-bottom wetlands of Migina catchment, southern Rwanda. *J. Environ. Manag.* **2018**, *219*, 103–114. [CrossRef]
83. Zorzal-Almeida, S.; Salim, A.; Andrade, M.R.M.; Nascimento, M.D.N.; Bini, L.M.; Bicudo, D.C. Effects of land use and spatial processes in water and surface sediment of tropical reservoirs at local and regional scales. *Sci. Total Environ.* **2018**, *644*, 237–246. [CrossRef]
84. Jiao, J.Y.; Wang, W.Z.; Jing, L.I. Effective cover rate of woodland and grassland for soil and water conservation. *Acta Phytoecol. Sin.* **2000**, *24*, 608–612.
85. Zhang, F.; Wang, J.; Xiaoping, W. Recognizing the Relationship between Spatial Patterns in Water Quality and Land-Use/Cover Types: A Case Study of the Jinghe Oasis in Xinjiang, China. *Water* **2018**, *10*, 646. [CrossRef]